14 Jul, 2006

Final Report for AOARD-05-4024

Ab initio direct trajectory simulation on hydrogen atom transfer in 7-azaindole in the electronic excited state with assist of water molecules

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I report here the results of three studies related to the AOARD project: (1) a direct trajectory simulation on the excited proton transfer in the 7-azaindole (7AI) assisted by water molecules, (2) a vibrational consistent-field study of vibrational spectrum of 7AI-H_2O, and (3) an ab initio study of reaction mechanism of double proton transfer in the 7AI-dimer in the excited states.

1. Ab initio direct trajectory simulation on the excited proton transfer in 7AI-$(H_2O)_2$

Recent developments in computational performance make it possible to combine ab initio electronic structure calculations with dynamics. In 1995, we implemented a dynamic reaction coordinate option in GAMESS, which enables one to carry out classical trajectory simulations for any molecular system in the electronic ground state, based on the energy gradients evaluated by ab initio molecular orbital calculations. The advantage of this approach is no requirement of potential energy functions in advance, while the disadvantage may be a large computational cost compared to the conventional trajectory calculations. Owing to the growth of performance of computer resources, however, the number of applications of this approach increases year by year, and it is now feasible to do direct trajectory simulations in the electronic ground state. The next stage is to develop a direct trajectory method for electronic excited states. In order to perform a trajectory simulation in electronic excited states, the energy gradients on the excited potential energy surface need to be evaluated. When the reaction proceeds only on a single excited potential energy surface, a state-specific multiconfigurational self-consistent field (MCSCF) method can be applied. If one considers the possibility of nonadiabatic transitions between two different potential energy surfaces, however, state-averaged MCSCF (SA-MCSCF) wavefunctions, or higher ab initio multireference theory, must be employed. Also, it is necessary to estimate the surface hopping probability for nonadiabatic transitions among the electronic states. In the present study, we have developed a program code for direct trajectory simulation in the electronic excited states which utilizes ab initio program package MOLPRO for electronic structure calculation parts. We also implemented an option for nonadiabatic surface hopping between adiabatic states, based on Tully's fewest switches algorithm (JCP **93**, 1061, 1990).

Our program code is applied to investigate the dynamical process of proton transfer in 7AI-$(H_2O)_n$ systems, i.e., a hydrogen atom transfer from a five-membered ring to a six-membered ring in 7AI assisted by water molecules, in the electronic excited states. The reaction paths for the H-transfer in 7AI and 7AI-H_2O systems in the ground and excited states were investigated by the multireference perturbation method by Chaban and Gordon (JPC A**103**, 185, 1999), and the activation energies for H-transfer in 7AI-$(H_2O)_n$ (n =

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
12 MAY 2007	**FInal**	**20-06-2005 to 17-07-2006**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Ab Initio Direct Trajectory Simulation on Hydrogen Atom Transfer in 7-azaindole in the Electronic Excited State with	**FA520905P0515**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Tetsuya Taketsugu**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Hokkaido University,Graduate School of Science,Sapporo 060-0810,Japan,JP,060-0810**	8. PERFORMING ORGANIZATION REPORT NUMBER **N/A**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AOARD, UNIT 45002, APO, AP, 96337-5002**	10. SPONSOR/MONITOR'S ACRONYM(S) **AOARD**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **AOARD-054024**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

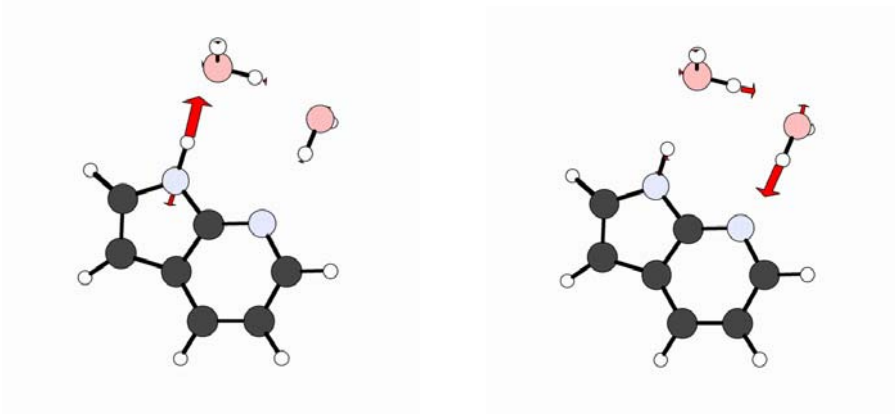
14. ABSTRACT
The work focused on the simulation of (1) direct trajectory on the excited proton transfer in the 7-azaindole (7AI) assisted by water molecules, (2) a vibrational consistent-field study of vibrational spectrum of 7AI-H2O, and (3) an ab initio study of reaction mechanism of double proton transfer in the 7AI-dimer in the excited states.

15. SUBJECT TERMS
ab initio Direct Dynamics, Modelling & Simulation, Electronic States

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**5**	

1-4) in the first excited state were also investigated by singly-excited configuration interaction (CIS) optimization and TD-DFT (B3LYP) energy calculations by Moreno et al. (CP, **290**, 319, 2003). In these studies, it was found that the presence of water molecules dramatically reduces the barrier to H-transfer in both electronic states, and the coordination of two water molecules is the most effective to lower the barrier of H-transfer in 7AI-$(H_2O)_n$ in the excited state. Thus, we decided to investigate the dynamics of H-transfer in 7AI-$(H_2O)_2$ in the present study.

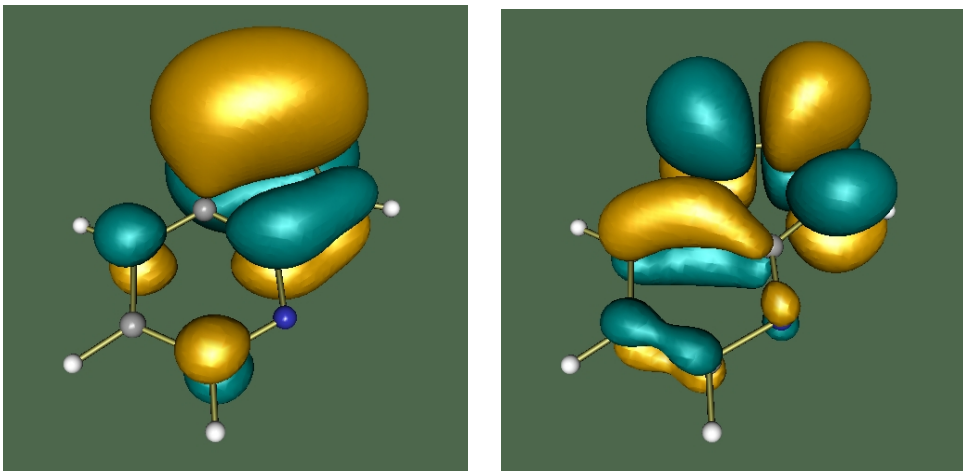
The molecular systems, 7AI plus two water molecules, make the complex with hydrogen bond network, and the H-transfer can occur through this network. Two H_2O molecules are referred to as $H_2O^{(6)}$ and $H_2O^{(5)}$ which coordinate to six- and five-membered rings of 7AI, respectively. First geometry optimization and normal mode analyses were carried out for 7AI-$(H_2O)_2$ in the ground state by the RHF method with Tatewaki's valence-double-zeta plus polarization (DZP) basis sets, and two normal modes have been picked up as the reaction modes which correspond to the N-H stretching mode in 7AI (3729 cm^{-1}) and the O-H stretching mode in $H_2O^{(6)}$ (3914 cm^{-1}), respectively. These two modes are shown in Fig. 1.



ν_1 = 3729 cm^{-1} ν_2 = 3914 cm^{-1}

Fig.1. Two normal modes related to H-transfer reaction.

The direct trajectory simulations were carried out for 7AI-$(H_2O)_2$ in the first-excited state by the state-averaged CASSCF (SA-CASSCF) method including two electronic states (ground and first excited states) and (2,2) active space with DZP basis sets. The active orbitals of HOMO and LUMO of 7AI molecule are shown in Fig. 2. As initial conditions, molecular geometry was started from the equilibrium structure in the ground state, vibrational energies were given to two reaction modes described above with quantum numbers (ν_1, ν_2), and then the molecular system was put on the potential energy surface of the first-excited state. The phases of vibrational motions of two reaction modes were determined to promote the H-transfer in 7AI most effectively. These conditions correspond to the excitation of specific vibrational modes related to the reaction. The trajectories starting with ν (= ν_1 = ν_2) = 0 ~ 5, as well as with zero initial kinetic energy, have been run with a fixed time step of 0.1 fs.



HOMO LUMO

Fig.2. HOMO and LUMO of 7-azaindole.

According to the results of direct trajectory simulations, it is shown that H-transfer in 7AI with H_2O is invoked in trajectories with $v \geq 3$. In these cases, N-H bond on five-membered ring of 7AI and O-H bond in $H_2O^{(5)}$ try to cleave simultaneously, and reach to the product side (7AI(tautomer)-$(H_2O)_2$), while H atom of $H_2O^{(6)}$ shows fluctuations between $H_2O^{(5)}$ and $H_2O^{(6)}$. No surface hopping was observed because of the large energy separation between the ground and excited states. Further investigations are necessary to examine the effects of intramolecular mode-mode couplings by providing zero-point vibrational energies to other degrees of freedom of 7AI fragment.

As the next step, we are developing a program code for the QM/MM excited direct trajectory simulation. In this code, the effective fragment potential (EFP) option (Day et al. JCP, **105**, 1968, 1996) in GAMESS is utilized as MM part, and some test calculations of EFP have already been finished to check the accuracy of static property such as the coordination structure, the intermolecular binding energy, and the excitation energy for the 7AI-H_2O system. By employing this program, we will add a larger number of EFP waters to investigate the effects of environmental water molecules on the H-transfer process. The results will be published in near future.

2. Vibrational analysis of 7AI-H_2O complex: anharmonicities using quartic force field

As the related work for 7AI-H_2O system, we have studied the vibrational spectra for 7AI and its tautomer, as well as the corresponding 7AI-H_2O systems, by the vibrational self-consistent field (VSCF) and correlation-corrected VSCF (cc-VSCF) methods combined with ab initio MP2 and DFT (B3LYP) calculations. To estimate the experimental fundamental frequencies quantitatively, the anharmonicity of the potential energy surface has been included by applying the quartic force field (QFF) approach implemented in Gamess by us (JCP, 121, **1383**, 2004). By using this option, one can estimate anharmonic vibrational frequencies for any polyatomic molecules with high accuracy. Figures 3 and 4 show several

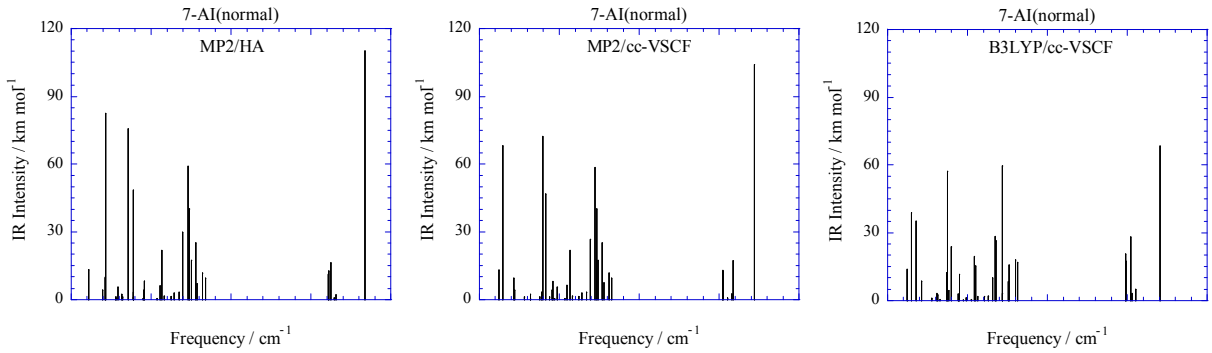


Fig. 3. Vibrational spectra for 7AI (normal) determined by MP2 (harmonic approximation (HA) and cc-VSCF/2MR-QFF) and B3LYP (cc-VSCF/2MR-QFF).

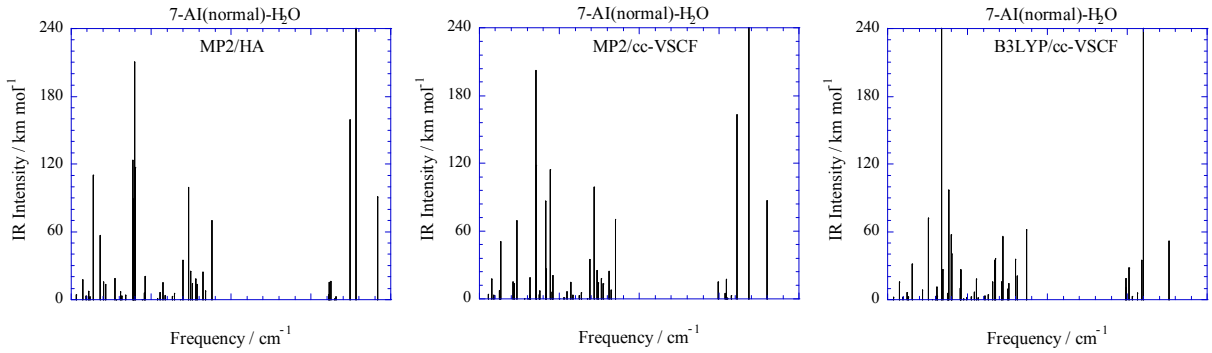


Fig. 4. Vibrational spectra for 7AI(normal)-H_2O complex determined by MP2 (harmonic approximation (HA) and cc-VSCF/2MR-QFF) and B3LYP (cc-VSCF/2MR-QFF).

calculated vibrational spectra for 7AI and 7AI-H_2O in normal form. At first glance, the two MP2 spectra look closer to each other than either does to the B3LYP spectrum. The intensity estimated by B3LYP is reduced in comparison with those obtained by MP2. By examining the first two MP2 spectra carefully, one can see the effects of anharmonicity and mode-mode couplings on the vibrational energy levels and intensities. There are observed several frequency shifts in the respective high frequency and low frequency regions.

The present VSCF / ab initio QFF applications to 7AI-H_2O system is the largest application among the previous studies, which needs a lot of nodes of computers to carry out these calculations in parallel. This study has been published in the special issue of Modeling of Vibrational Spectroscopies (Taketsugu et al. IJQC, **104**, 758-772, 2005).

3. Ab initio study on reaction mechanism of double proton transfer in 7AI-dimer in excited states

We have not yet started, but we have a plan to extend ab initio direct dynamics study to the 7AI-dimer + H_2O system which was studied experimentally through femtosecond pump-probe techniques by Castleman et al. (PNAS, **96**, 12980, 1999). They proposed that the excited double-proton transfer in the 7AI-dimer accompanying the structure transformation from normal to tautomer occurs in a stepwise manner, while some other groups insisted that this process occurs in a concerted manner. In order to clarify this reaction mechanism from theoretical viewpoint, we have carried out ab initio SA-CASSCF calculations with the 6-31G(d) basis sets to locate stationary points on the potential energy surfaces related to the excited double proton transfer in 7AI-dimer. The SA-CASSCF calculations include the (8,8) active space of π orbitals, and ground and two lowest excited states were averaged with equal weights since the first- and second-excited states of 7AI-dimer correspond to the combinations of the ground and first-excited states of the respective 7AI monomers with in-phase and anti-phase, respectively, and thus these two states are nearly degenerate with each other. We have located equilibrium structures of 7AI-dimer of normal and tautomer structures (C_{2h}), as well as the intermediate structure (C_s), in the first-excited state. Our calculations suggest that the double proton transfer proceeds via the intermediate structure, supporting the stepwise mechanism. Following the static analyses of potential energy surfaces of the excited states, we continue to investigate the dynamics of this process by the ab initio direct trajectory approach, in which solvent water molecules are also included in the simulations using an EFP option.